



# Cu-SSZ-13 as pre-turbine NO<sub>x</sub>-removal-catalyst: Impact of pressure and catalyst poisons



Tobias Günter, Jan Pesek, Kathrin Schäfer, Anna Bertótiné Abai, Maria Casapu, Olaf Deutschmann, Jan-Dierk Grunwaldt\*

*Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology, D-76131 Karlsruhe, Germany*

## ARTICLE INFO

### Article history:

Received 15 March 2016

Received in revised form 27 May 2016

Accepted 2 June 2016

Available online 3 June 2016

### Keywords:

Selective catalytic reduction

Cu-SSZ-13

Poisoning

Pre-turbo

High pressure

## ABSTRACT

The development of highly efficient engines with lower exhaust gas temperatures leads to new challenges for catalysts in the aftertreatment system. One option for overcoming this is a catalyst positioned in front of the turbocharger with an exposure to higher temperature and pressure. The impact of increased pressure and typical catalyst poisons on the catalytic performance of a state-of-the-art Cu-SSZ-13 catalyst has thus been studied during the selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub>. Various reactions including NO/NH<sub>3</sub> oxidation, standard and fast SCR have been tested in a temperature range of 180–600 °C. Propene as representative for small hydrocarbons and SO<sub>2</sub> have been added under reaction conditions to analyze the direct influence at relevant reaction temperatures. An increased pressure resulted in a strikingly higher DeNO<sub>x</sub>-activity especially under Standard-SCR conditions, which was mainly due to higher NO oxidation to NO<sub>2</sub> in the gas phase and a higher residence time. Even though propene led to a temporary competition between SCR-reaction and propene oxidation, the small decrease in DeNO<sub>x</sub>-activity can be overcompensated by the higher pressure and temperature within a pre-turbine configuration with no need for regeneration steps. In contrast, SO<sub>2</sub> caused severe deactivation at low temperature but no influence at high temperature. Reactivation was not completely possible, which suggests some highly stable sulfur species. The higher pre-turbine temperature enables an earlier regeneration, showing a further advantage of pre-Turbo-SCR.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

The application of catalysts in various emission control technologies has led to decreased air pollution by road traffic over the last decades. More stringent emission standards have been launched lately, focusing especially on NO<sub>x</sub> and particulate matter. Selective catalytic reduction (SCR) of NO<sub>x</sub> using NH<sub>3</sub> has become a leading technique in mobile applications [1,2]. The identification of the copper-exchanged zeolite Cu-SSZ-13 as a high potential catalyst with high activity at low temperature and good hydrothermal stability has resulted in an increased research effort to optimize catalytic activity and synthesis cost, as well as numerous approaches to understand aspects of the reaction mechanism [3–9]. Taking the step from typical model conditions towards application requires a holistic view on the exhaust gas aftertreatment system, including the gas composition at different positions and under various

driving conditions. The development of more efficient engines as well as the extensive use of exhaust gas recirculation (EGR) results in lower exhaust gas temperatures that are more often below the operating range of the catalyst. One way to circumvent this situation is to position the catalyst closer to the engine, in front of the turbocharger. This option has been tested for diesel oxidation catalysts, diesel particulate filters and recently also for vanadium-based SCR-catalysts [10,11]. Usually, the turbocharger is installed between the engine and the catalysts and therefore it is exposed to 100–150 °C higher temperature. An implementation of catalysts in front of the turbocharger would thus result in an earlier light-off. As a further benefit, the pressure built-up from the turbocharger (typically up to 5 bar [10–12]) would lead to an increased residence time of the reactants at the catalyst, which would make a smaller total catalyst size possible as well as a decreased back-pressure penalty [11,13]. This is also supported by numerical simulations by Subramaniam et al. [13], who studied a pre-turbine placement of the entire aftertreatment system for a large bore diesel engine and predicted a reduction of the catalyst volume >40% and some decreased fuel consumption. Kröcher et al. [11] reported that a

\* Corresponding author.

E-mail address: [grunwaldt@kit.edu](mailto:grunwaldt@kit.edu) (J.-D. Grunwaldt).

pressure increase by a factor of two combined with half the catalyst size did not result in the same catalytic activity but a slightly lower one, probably due to diffusion limitations. While the residence time is proportional to the pressure at a given mass flow rate, the diffusivity is proportional to the reciprocal of the pressure. The resulting impact of both processes consequently depends on the operating conditions. In general, kinetics is more significant at lower temperature, while diffusion limitations are more significant at higher temperature and long diffusion lengths. Hence, the geometrical structure of the catalyst may reduce the negative impact of pressure on diffusion and consequently conversion, e.g. by using thinner channels. However, the latter one will increase the pressure drop. The impact of a pressure drop at the catalyst during an implementation upstream of the turbocharger would be smaller than in a downstream configuration, and therefore a positive influence on the efficiency of the turbocharger is expected [14,15].

One drawback for passenger cars are quick load changes accompanied by pressure changes that cause mechanical stress at the catalyst. This effect is less pronounced in larger applications with close to steady-state conditions, like in trains and ships. However, a systematic understanding of a catalyst positioned in front of the turbocharger is first needed before focusing on technical details.

A pre-turbine position of the SCR-catalyst without rearranging the other catalysts (e.g. Diesel oxidation catalyst (DOC) and Diesel particulate filter (DPF)) would result in an exposure to higher amounts of unburned hydrocarbons, particulate matter and less  $\text{NO}_2$ . The latter supports the so-called Fast-SCR reaction, while the hydrocarbons may deposit as coke on the zeolite surface or enter the pores, depending on the size [16]. Particulate matter is usually too large to enter the zeolite pores but can also be converted [17]. Note that it can also negatively affect the performance by fouling the catalyst surface. In addition, the conversion of the  $\text{NO}_x$  at the SCR catalyst would result in less  $\text{NO}_2$  at the DPF, lowering the passive soot oxidation and making a higher active regeneration frequency necessary [18]. Also unburned hydrocarbons lead to a more pronounced poisoning effect on medium-pore sized Cu-ZSM-5 compared to the small-pore sized Cu-SSZ-13 [19]. In all cases, the entering hydrocarbons may adsorb in competition with  $\text{NH}_3$  and  $\text{NO}_x$ , and therefore hinder the SCR-reaction [20,21]. This adsorption does not only occur on the acidic sites but also on the catalytically active Cu-sites [22] and shows a dependency on the concentration and type of hydrocarbons [23]. The higher temperature and pressure present upstream of the turbocharger might compensate the poisoning effect of the hydrocarbons and needs to be investigated.

Furthermore, sulfur is always present in exhaust gas, originating from the fuel or lubricants. Although its concentration in the fuel is limited, zeolite based DeNO<sub>x</sub>-catalysts are sensitive to this small amount. The  $\text{SO}_2/\text{SO}_3$  ratio as well as the temperature, at which the poisoning was performed, influences the degree of deactivation [24,25]. The formation of  $\text{CuSO}_x$  has been proposed resulting in a lower amount of SCR-active sites [26]. In addition, at low temperatures  $(\text{NH}_4)_2\text{SO}_4$  is formed, which can block the pores and the active sites [27]. For a possible pre-turbine application, the poisoning effect of sulfur also needs to be tested at increased pressure.

In this paper, we present a first study on the influence of pressure on the catalytic activity of a zeolite-based catalyst during the SCR-reaction and related conditions to test a possible application of Cu-SSZ-13 closer to the engine at higher temperature and pressure. The effect of propene as small hydrocarbon molecule on the SCR-activity as well as its oxidation under ambient and increased pressure is shown. Furthermore, the impact of the catalyst poison sulfur at different pressures on the SCR-reaction is examined. The regeneration ability for both poisons was investigated to evaluate the temporary and permanent effects on the catalyst.

## 2. Experimental

### 2.1. Catalyst preparation

For the study a Cu-SSZ-13 zeolite ( $\text{Si}/\text{Al}=16$ ) with a copper loading of 1.2 wt.% was used. The catalyst was synthesized and characterized as described in our earlier study [9]. Then a dip-coating technique was used to coat the catalyst on a cordierite monolith (cell density of 400 cpsi). For the catalytic tests, a piece of 2.54 cm diameter and 3 cm length was taken. The catalyst slurry was prepared by mixing 5 g Cu-SSZ-13 with 30 ml demineralized water and 0.75 ml Ludox AS-40 (colloidal silica solution) as binder. The dipping and drying process was repeated several times until the desired loading was achieved. The coated honeycomb was calcined in air at 550 °C for 8 h, resulting in a total coating of 2.23 g ( $2.4 \text{ g}/\text{in}^3$ ). In order to evaluate a possible long term deactivation at higher pressure the same honeycomb was used for the entire study without replacement. Over the complete study, the weight loss of the coated cordierite core was only about 3 wt.%.

### 2.2. Catalyst characterization

The Cu-SSZ-13 catalyst was thoroughly characterized as powder before coating. This ensured that we use a Cu-SSZ-13 catalyst that is the present state of the art and similar to the one used in previous studies [9,28].

X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance diffractometer using Cu  $K\alpha$  radiation. The scans were recorded in a  $2\theta$  range of 5–50° with steps of 0.016°. H-SSZ-13 and Cu-SSZ-13 show the characteristic diffraction patterns of chabazite lattice and no additional reflections after the Cu exchange.

X-ray absorption spectroscopy (XAS, EXAFS) data were acquired for Cu K edge at ANKA (Karlsruhe, Germany). The pelletized sample, copper oxide and foil references were measured in transmission mode. The analysis of the X-ray absorption near edge structure (XANES) and of the Extended X-Ray Absorption Fine Structure (EXAFS) was performed using the Athena software from the IFFEFIT package [29]. The Fourier Transform EXAFS spectrum confirmed the high dispersion of Cu and suggests the presence of mainly isolated 4-fold coordinated  $\text{Cu}^{2+}$ -sites [9].

The elemental composition was determined by X-ray fluorescence (XRF) at the Institute for Applied Materials – Applied Materials Physics (IAM-AWP, KIT). The studied catalyst contains 1.2 wt.% Cu, 93 wt.%  $\text{SiO}_2$  and 5.0 wt.%  $\text{Al}_2\text{O}_3$ , corresponding to a Si:Al ratio of 16:1 and a molar Cu ion exchange degree ( $\text{Cu}/\text{Al}_2$ ) of 0.4. A Belsorp Mini II (Bel Japan Inc.) was used to measure the BET surface area and pore volume, which amount to  $590 \text{ m}^2/\text{g}$  and a total pore volume of  $0.33 \text{ cm}^3/\text{g}$ , respectively [9].

### 2.3. Test bench setup

Catalytic tests were performed in a fixed-bed stainless steel reactor dedicated for experiments at increased pressure and in the presence of  $\text{SO}_x$ -compounds. All parts, which are exposed to  $\text{SO}_x$ , were coated with a sulfur-inert/corrosion resistant layer (SilcoTek). The evolved gases were analyzed using an MKS Multigas 2030 FTIR spectrometer equipped with ZnSe-windows. A total flow of 12.67 l/min was used, corresponding to a space velocity of  $50,000 \text{ h}^{-1}$ .

Prior to each experimental sequence, the coated catalyst was heated to 600 °C in 10%  $\text{O}_2$ , 5%  $\text{H}_2\text{O}$  and  $\text{N}_2$  to remove adsorbates and ensure equivalent conditions. After conditioning for 1 h under the SCR stream at 1 bar, the SCR reactions without  $\text{C}_3\text{H}_6$  and  $\text{SO}_2$  were performed, starting at 600 °C with NO-oxidation (500 ppm NO), Standard-SCR (500 ppm NO, 500 ppm  $\text{NH}_3$ ),  $\text{NH}_3$ -oxidation

(500 ppm  $\text{NH}_3$ ) and Fast-SCR (250 ppm NO, 250 ppm  $\text{NO}_2$ , 500 ppm  $\text{NH}_3$ ) (all conditions with 10%  $\text{O}_2$ , 5%  $\text{H}_2\text{O}$ ,  $\text{N}_2$  balance). The reactions were conducted until steady-state conditions were reached before switching to the next gas mixture. Note that the performance was determined starting at the highest temperature and cooling down stepwise by 50 °C steps to 180 °C. This protocol was repeated at atmospheric pressure, 2, 4 and 5 bar. Next, a second complete measurement was performed following the same protocol to evaluate the extent of catalyst deactivation upon 120 h testing under the SCR stream at high pressures and at temperatures up to 600 °C. The resulting sample was considered as the degreened catalyst and it has been used as reference for the next tests.

After the tests on influence of pressure, the experiments on the additional impact of  $\text{C}_3\text{H}_6$  were performed on the same cordierite coated catalyst sample. The  $\text{C}_3\text{H}_6$ -oxidation (500 ppm  $\text{C}_3\text{H}_6$ , 10%  $\text{O}_2$ , 5%  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ) was measured with the same temperature and pressure protocol as the experiments described above. The impact of  $\text{C}_3\text{H}_6$  on the Standard-SCR-reaction (200 ppm  $\text{C}_3\text{H}_6$ , 500 ppm NO, 500 ppm  $\text{NH}_3$ , 10%  $\text{O}_2$ , 5%  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ) and Fast-SCR-reaction (200 ppm  $\text{C}_3\text{H}_6$ , 250 ppm NO, 250 ppm  $\text{NO}_2$ , 500 ppm  $\text{NH}_3$ , 10%  $\text{O}_2$ , 5%  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ) was tested by measuring the gas concentrations at each temperature under reaction conditions without  $\text{C}_3\text{H}_6$ , followed by 60 min with  $\text{C}_3\text{H}_6$  and a third step without  $\text{C}_3\text{H}_6$  again.

The effect of  $\text{SO}_2$  on the Standard-SCR-reaction and a possible regeneration was tested by performing one complete temperature run from 600 °C to 180 °C dosing 20 ppm  $\text{SO}_2$  under Standard-SCR-conditions followed by a DeSOx-step (heating to 600 °C in 10%  $\text{O}_2$ , 5%  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ) and the same temperature run under Standard-SCR-conditions without  $\text{SO}_2$ . This procedure was repeated at 2, 4 and 5 bar.

As gas phase reactions are expected at high temperatures especially under high pressure, all reaction conditions were also tested in the empty reactor. The results were compared to simulation (cf. Section 2.4).

Mass-transfer limitation in the washcoat was tested by varying the thickness of the monolith coating layer. The ratio of flow-rate to amount of Cu-SSZ-13 was kept constant. Both catalysts showed the same activity, excluding transport limitations in the washcoat under the applied conditions.

## 2.4. Kinetic simulations

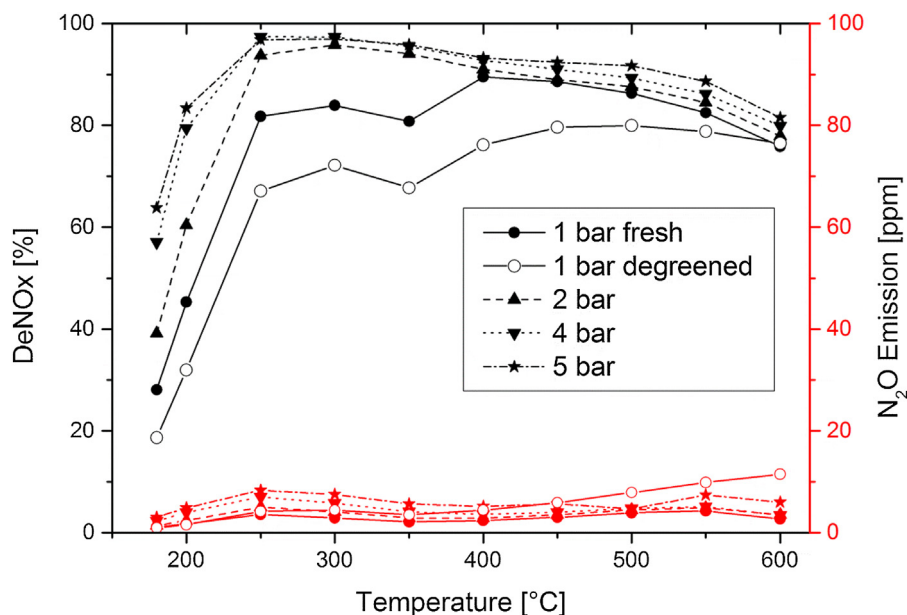
For kinetic simulations of the reactions in the gas-phase, the numerical simulation package DETCHEM [30] was applied. The simulations were executed with the batch reactor model. The length of the reactor with taking into account gas velocity, temperature- and pressure profiles was converted to residence time as a model parameter. The batch model calculated homogeneous gas phase reactions at given temporal temperature and pressure profiles assuming perfect mixing of the gases. The used kinetic mechanism is based on Konnov [31,32] and Warnatz [33] mechanisms, containing 31 species and 245 elementary reactions.

## 3. Results and discussion

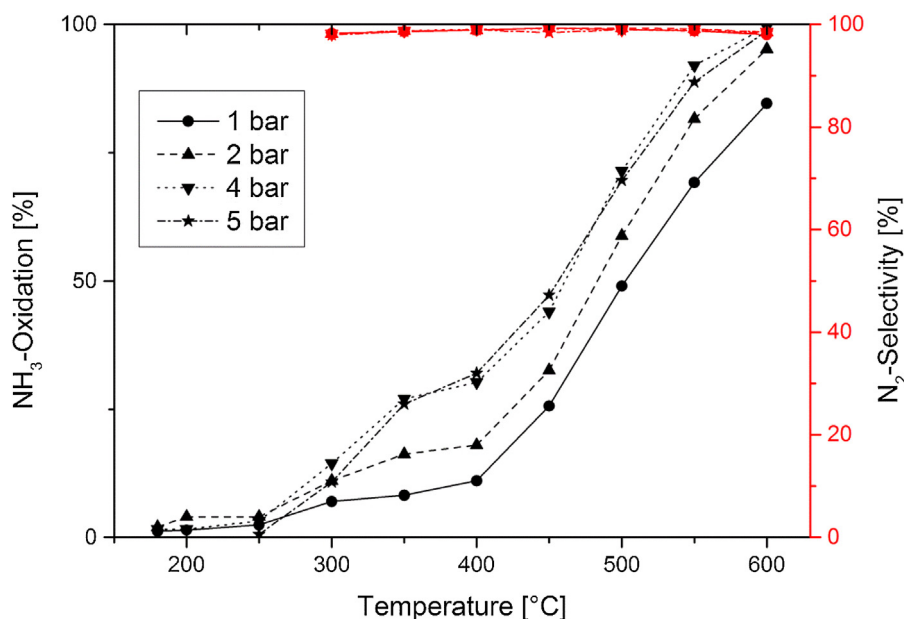
### 3.1. Influence of pressure on the SCR-reaction

The testing procedure included the evaluation of the standard and fast SCR,  $\text{NH}_3$  oxidation and NO oxidation reactions at different pressure between 1 and 5 bar in the temperature range 180–600 °C (series conducted twice for uncovering possible deactivation effects, see experimental part). Fig. 1 shows the DeNOx-activity of the as prepared catalysts (conditioned for 1 h at 600 °C under the SCR gas mixture) in terms of  $\text{NO}_x$ -conversion under Standard-SCR conditions at different pressures up to 5 bar and also includes the formation of  $\text{N}_2\text{O}$ . At ambient pressure, a typical activity profile is observed, showing good SCR-activity over a broad temperature range. At low temperatures, the conversion is restricted by the kinetic limitation, whereas the slight activity decrease at higher temperatures can be explained by side reactions, such as  $\text{NH}_3$  oxidation, which has been investigated separately (Fig. 2). The activity drop around 350 °C has been reported before as the seagull shape effect and was correlated with different reaction mechanisms or active sites for the low and high temperature regime [5,7,34]. The selectivity towards formation of  $\text{N}_2\text{O}$  is below 5 ppm at all temperatures.

Increasing the pressure to 2, 4 or 5 bar results in significant changes of the catalytic performance. The catalytic activity increases over the entire temperature range with increasing pres-



**Fig. 1.** Standard-SCR activity (left, black) and  $\text{N}_2\text{O}$  formation (right, red) at different pressures; solid line – 1 bar, dashed line – 2 bar, dotted line – 4 bar, dash-dotted line – 5 bar. Feed: 500 ppm NO, 500 ppm  $\text{NH}_3$ , 10%  $\text{O}_2$ , 5%  $\text{H}_2\text{O}$  in  $\text{N}_2$ . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 2.** NH<sub>3</sub>-Oxidation activity (left, black) and selectivity towards N<sub>2</sub>-formation (right, red) at different pressures; solid line – 1 bar, dashed line – 2 bar, dotted line – 4 bar, dash-dotted line – 5 bar. Feed: 500 ppm NH<sub>3</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O in N<sub>2</sub>. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

sure. This effect is more pronounced at low temperatures up to 250 °C, where 2 bar is enough to reach almost full conversion. This can be explained by an increased residence time of the reactants at the catalyst. At high temperatures, the positive influence of a higher pressure indicates a better selectivity towards the SCR-reaction instead of side reactions, e.g. NH<sub>3</sub>-oxidation.

The results of the second complete SCR test indicated that under the gas stream, pressure and temperature conditions applied in this study the Cu-SSZ-13 catalyst undergoes a moderate deactivation. A decrease of about 10% in NO<sub>x</sub>-conversion was measured at atmospheric pressure for the standard SCR reaction at all temperatures. For the tested GHSV, the deactivation was not noticeable at higher pressures (not shown). Although at temperatures below 600 °C thermal deactivation of the Cu-SSZ-13 is not expected, the special testing procedure used here which includes high pressure and the complete SCR mixture (not only H<sub>2</sub>O vapors) could lead to Cu migration or to zeolite dealumination, and need to be investigated in further studies. The activity obtained in the second complete test is referred in the following as the SCR performance of the degreened Cu-SSZ-13.

As the empty reactor tests showed, the main reason for the overall catalytic improvement at higher pressures is the increased NO-oxidation rate in the gas phase producing NO<sub>2</sub> (Fig. 3). It occurs to almost the same extent over the catalyst and in the empty reactor. Only at elevated temperature the catalyst further promotes NO-oxidation. This improved gas phase oxidation of NO to NO<sub>2</sub> at elevated pressure was additionally confirmed by numerical simulations of gas phase reactions, which qualitatively agree with measurements in the empty reactor (Fig. 3, blue and red line), ruling out possible contributions of the reactor wall. Therefore, only reactions in the gas phase and on the catalyst contribute to the measured results. Calculations of equilibrium composition depending on temperature and pressure (Fig. S1) showed that the system is far from equilibrium composition at any investigated pressure and reactor temperature, proving that NO-oxidation is kinetically limited. Gas phase reactions thus play an important role in the reactor and will be reported in more detail in a forthcoming study.

As NO<sub>2</sub> is available in the gas phase at increased pressure, Standard- and Fast-SCR-reaction will occur in parallel even though

only NO is dosed, which has a strong effect on the low temperature part of SCR-performance at elevated pressure (Fig. 1). The seagull-shaped profile cannot be observed any more, probably due to the high conversion at the GHSV applied in this study. Regarding the N<sub>2</sub>O emissions, even though the formation of N<sub>2</sub>O increases at higher pressures the maximum remains below 10 ppm.

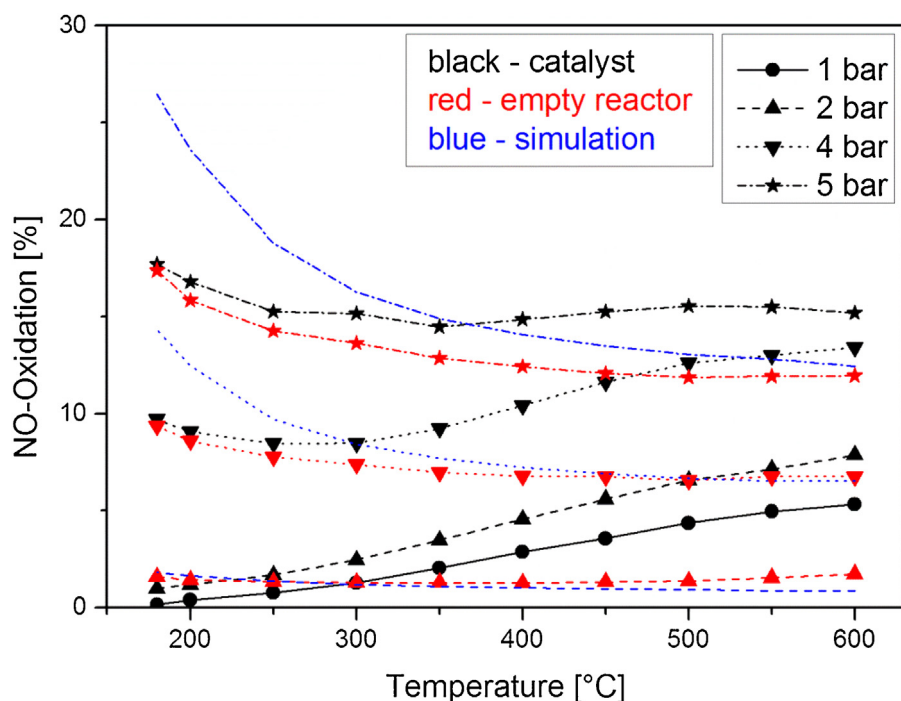
A less pronounced effect of the pressure is observed under Fast-SCR conditions, as depicted in Fig. 4. Higher pressure leads only to a slight increase of activity, probably due to increased residence time, at low temperatures and full conversion is reached at 250 °C at all pressures. In contrast to the Standard-SCR reaction, starting from 500 °C the increase of pressure leads to a slightly lower DeNO<sub>x</sub>-activity. This is probably due to the NO<sub>2</sub> induced gas phase reactions which negatively influence the catalytic activity (Fig. S2). Particularly, the NH<sub>3</sub>-conversion increases at higher pressure and temperature when compared to standard SCR conditions, which can be correlated to oxidation by NO<sub>2</sub>, leading to N<sub>2</sub> and NO formation according to Watling et al. [35]. As temperatures above 500 °C are less relevant under real driving conditions, even under pre-turbo configuration, the contribution of these gas phase reactions is negligible [36].

### 3.2. Interaction with propene

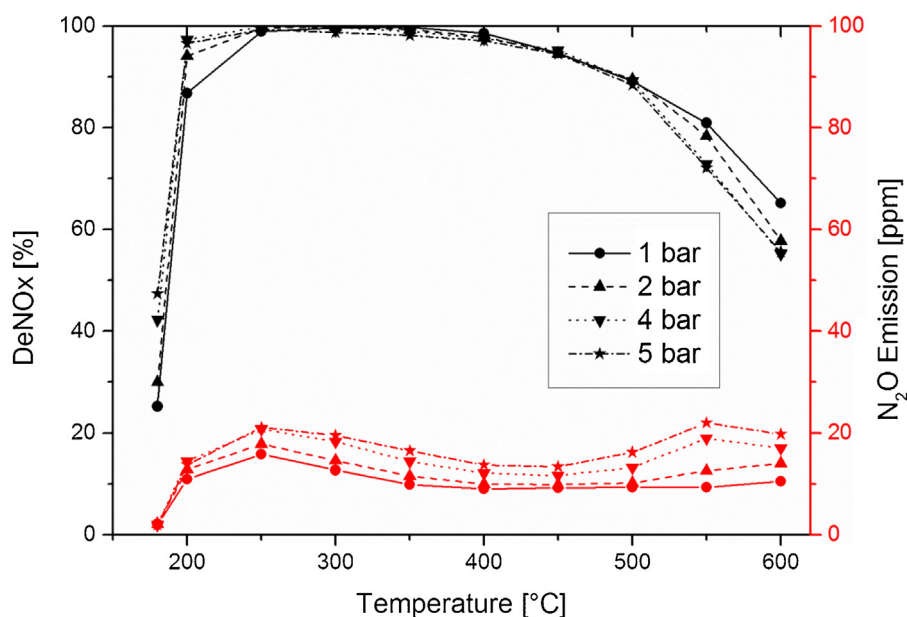
#### 3.2.1. Propene oxidation

Installing the SCR-catalyst in front of the turbocharger would result in an exposure to all emissions from the engine, as other catalysts like the Diesel oxidation catalyst or particulate filter are usually placed further downstream. As probe molecule for the interaction of unburned hydrocarbons C<sub>3</sub>H<sub>6</sub> was taken (500 ppm) in addition to the SCR stream. Its catalytic oxidation has to be studied separately in addition to the influence on the SCR-reaction in order to understand interactions with the SCR-relevant gases. Hence, the reaction was monitored in a stepwise manner followed by a temperature programmed oxidation (TPO) step after the test run to monitor the release and oxidation of the adsorbed C<sub>3</sub>H<sub>6</sub>-derived species. The oxidation of propene over the Cu-SSZ-13 catalyst without SCR-conditions starts already at low temperatures, but a full conversion is not obtained, even at 550 °C (68% converted)





**Fig. 3.** NO-Oxidation activity at different pressures with catalyst and in empty reactor (experimental and simulated); solid line – 1 bar, dashed line – 2 bar, dotted line – 4 bar, dash-dotted line – 5 bar. Feed: 500 ppm NO, 10% O<sub>2</sub>, 5% H<sub>2</sub>O in N<sub>2</sub>. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

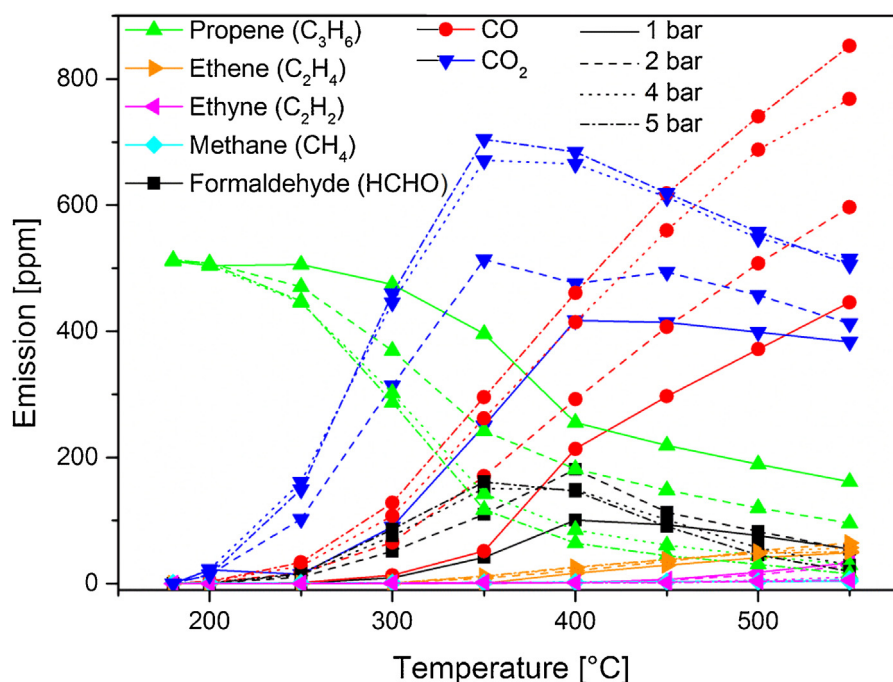


**Fig. 4.** Fast-SCR activity (left, black) and N<sub>2</sub>O formation (right, red) at different pressures; solid line – 1 bar, dashed line – 2 bar, dotted line – 4 bar, dash-dotted line – 5 bar. Feed: 250 ppm NO, 250 ppm NO<sub>2</sub>, 500 ppm NH<sub>3</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O in N<sub>2</sub>. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

as shown in Fig. 5. CO and CO<sub>2</sub> are the main products with CO being favored at higher temperatures. The maximum of CO<sub>2</sub> production is reached at around 350–400 °C. In this temperature range, formaldehyde was additionally produced by partial oxidation of propene (up to 100 ppm formaldehyde recorded at 400 °C). As further side products, low amounts of methane, ethene and ethyne were observed with increasing the temperature (<50 ppm).

Increasing the pressure from 1 bar to 2 bar or 4 bar leads to a significantly higher conversion of propene, whereas a further increase

to 5 bar resulted only in a small change as compared to 4 bar. Thus, the conversion at 350 °C shows a clear improvement from 23% at 1 bar to 53% (2 bar) and 72% (4 bar), but only a small change to 77% at 5 bar. The main products are still CO and CO<sub>2</sub> with a slightly lower selectivity towards CO<sub>2</sub> at increased pressure. The emission of formaldehyde is intensified at elevated pressure (160 ppm at 5 bar and 350 °C) which is in line with higher C<sub>3</sub>H<sub>6</sub> conversion. The TPO-results obtained after exposing the catalyst to the C<sub>3</sub>H<sub>6</sub>-O<sub>2</sub> gas mixture at 180 °C, are shown in Fig. S4 and uncover the desorption



**Fig. 5.** Emission of carbonaceous compounds from partial and total oxidation of propene of the degreened Cu-SSZ-13; solid line – 1 bar, dashed line – 2 bar, dotted line – 4 bar, dash-dotted line – 5 bar. Feed 500 ppm  $C_3H_6$ , 10%  $O_2$ , 5%  $H_2O$ ,  $N_2$ .  $CO_2$  concentration calculated from C-balance.

of small traces of CO and formaldehyde (detection of  $CO_2$  was not possible) with no clear dependency of the total amount of the desorbed species on the applied pressure. This observation indicates that the amount of deposition on the catalyst is independent from the pressure.

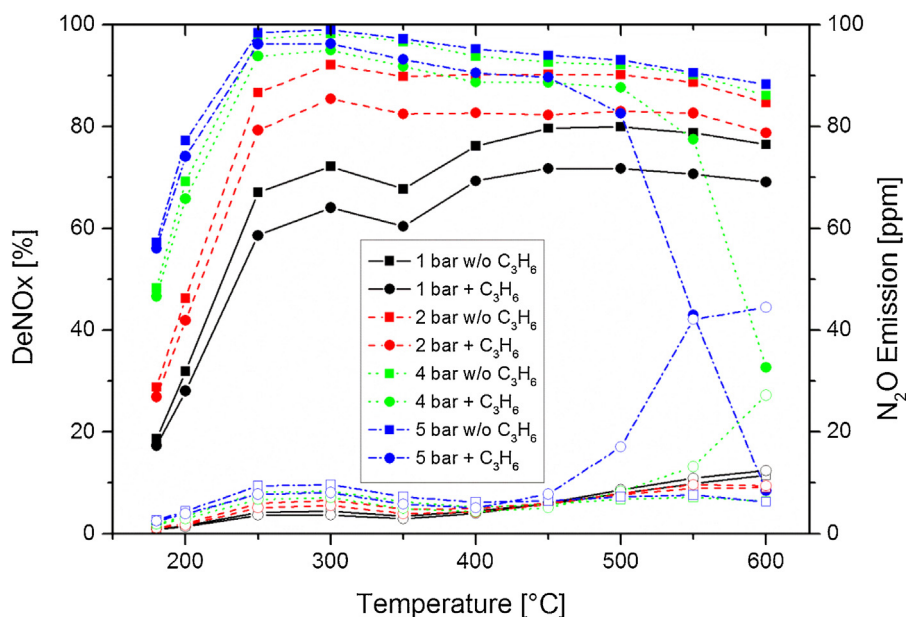
### 3.2.2. Effect of propene on SCR-activity

At each temperature, the SCR-activity was measured first without  $C_3H_6$ , second while dosing  $C_3H_6$  and third followed by a measurement without  $C_3H_6$  again, before decreasing the temperature to the next measurement point. By using this procedure, a possible permanent poisoning could be checked at each temperature additionally to the temporary effect of  $C_3H_6$ . The DeNOx-activity measured at steady-state conditions before and after dosing  $C_3H_6$  was the same at all temperatures and pressures. This corresponds to the activity of the degreened Cu-SSZ-13 catalyst (Fig. 1). Hence, the possible adsorbed species at low temperatures (after  $C_3H_6$  dosage step) have no influence on the SCR-activity as they are most probably easily replaced by  $NO_x$  [21]. A direct comparison of the Standard-SCR-activity with and without dosing  $C_3H_6$  (Fig. 6) showed an almost constant drop in activity of 6–8% from 250 to 600 °C at low pressures (<3 bar). During the SCR-reaction over the catalyst, propene is catalytically oxidized (Fig. 7) in a similar manner to the  $C_3H_6$ -oxidation in Fig. 5. This catalytic process might occur at the same sites as the SCR-reaction and could explain the decrease in DeNOx-activity by a competing adsorption of  $C_3H_6$  and SCR-related species. An influence on the formation of  $N_2O$  is negligible at these pressures. Up to 450 °C, increasing the pressure to 4 and 5 bar results in a lower impact of  $C_3H_6$  on the SCR-activity.

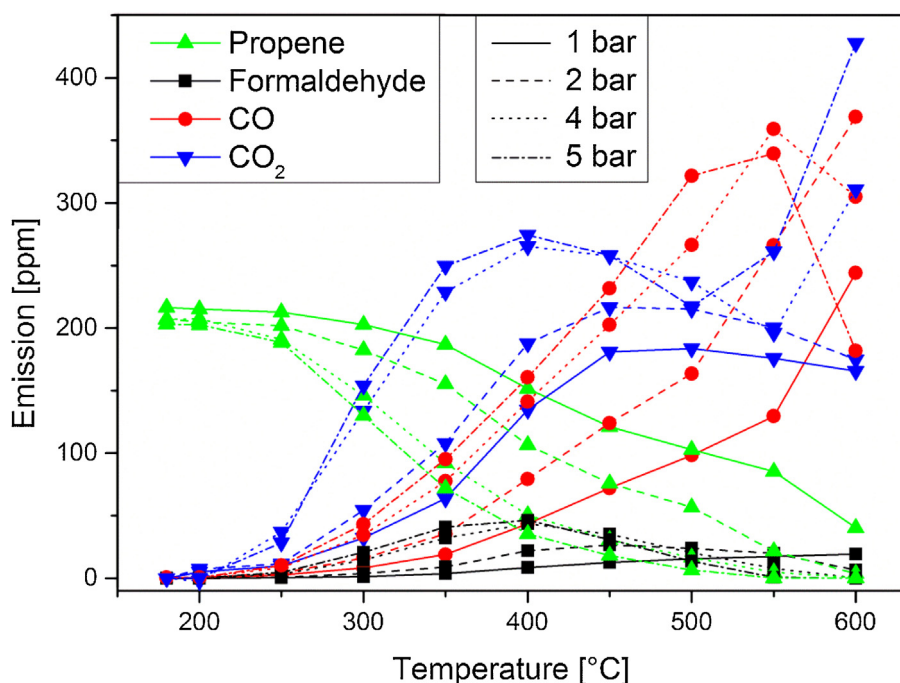
Despite there is some lower DeNOx-activity without propene at ambient pressure at elevated pressure the performance is much better. The additional pressure overcompensates the deactivating effect of propene. Also in the presence of propene the seagull shaped profile is not visible and apart from the higher residence time the gas-phase formed  $NO_2$  obviously has a beneficial effect on the catalytic performance.

Starting at 500 °C, the DeNOx-activity at 4 and 5 bar decreases drastically with an increased formation of  $N_2O$ . For the same pressure and temperature region this behavior was also observed with the empty reactor, while checking for possible gas phase reactions. In the empty reactor, the concentrations of NO and  $NH_3$  decrease, while  $NO_2$  is formed. At this temperature propene also starts to react, forming mainly CO and  $CO_2$  (Fig. S3). Some of these species and especially the reactive radicals which are formed during  $C_3H_6$  oxidation are known to promote NO to  $NO_2$  oxidation at high temperatures [37,38].  $NH_3$  oxidation by  $NO_2$  is additionally promoted in propene containing gas mixture leading to complete consumption of  $NH_3$  at 600 °C at 5 bar (Fig. S5). These gas phase reactions, which occur in parallel to the desired SCR-reaction, lead to the observed drop of the catalytic DeNOx-activity at high temperatures for 4 and 5 bar. Even though this activity decrease at high temperature and pressure is undesired, it is less relevant under real driving conditions.

The influence of  $C_3H_6$  addition on the Fast-SCR gas mixture (Fig. 8) is analogous to that observed for Standard-SCR but with a more pronounced impact of gas phase reactions at high temperatures. The DeNOx-activity at low temperatures is less affected under Fast-SCR-conditions than under Standard-SCR-conditions. Starting from 450 °C, the DeNOx-activity decreases especially at high pressures combined with an increased formation of  $N_2O$ . In this temperature and pressure range,  $C_3H_6$  is strongly oxidized mainly to CO,  $CO_2$  and formaldehyde (Fig. 9). In the gas phase,  $NH_3$ -oxidation and  $C_3H_6$ -oxidation start at around the same temperature (>350 °C, Figs. S7 and S8). In this light-off region, NO is converted to  $NO_2$  and  $NH_3$  is oxidized unselectively to  $N_2$ ,  $N_2O$  and  $NO_x$ , which is evidenced by an increase of the total  $NO_x$ -concentration. Its oxidation is more pronounced in the presence of  $C_3H_6$ , compared to the carbon-free conditions, suggesting once again a promoting effect for the formation of free radicals. This is supported by literature, where oxidation of propene to acrolein on Cu-SSZ-13 has been observed with DRIFTS at 350 °C and ambient pressure [21] and even gas phase oxidation to e.g. propene oxide is known at higher pressure [39]. Formed radicals promote the NO-



**Fig. 6.** Standard-SCR activity (left, filled symbols) and N<sub>2</sub>O formation (right, open symbols) of the degreened Cu-SSZ-13 with and without dosing C<sub>3</sub>H<sub>6</sub>; solid line – 1 bar, dashed line – 2 bar, dotted line – 4 bar, dash-dotted line – 5 bar. Feed: 0/200 ppm C<sub>3</sub>H<sub>6</sub>, 500 ppm NO, 500 ppm NH<sub>3</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O in N<sub>2</sub>.



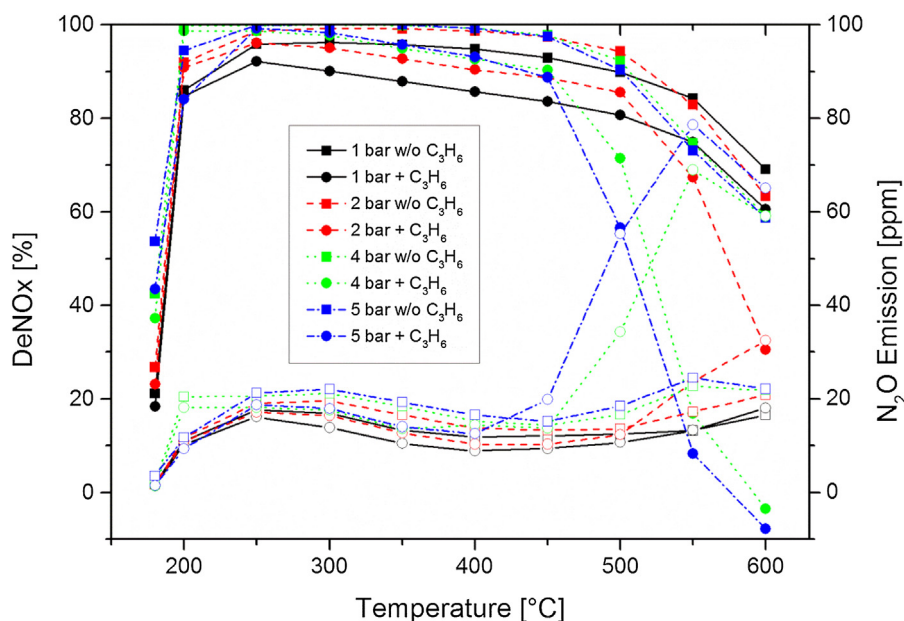
**Fig. 7.** Emission of carbonaceous compounds during Standard-SCR with C<sub>3</sub>H<sub>6</sub> of the degreened Cu-SSZ-13; solid line – 1 bar, dashed line – 2 bar, dotted line – 4 bar, dash-dotted line – 5 bar. Feed: 200 ppm C<sub>3</sub>H<sub>6</sub>, 500 ppm NO, 500 ppm NH<sub>3</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O in N<sub>2</sub>. CO<sub>2</sub> concentration calculated from C-balance.

oxidation and break up propene to produce more C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> radicals, accelerating radical dominated unselective reactions [37,40]. This shows the complexity of the interaction of the SCR-mixture with hydrocarbons especially at higher temperature and pressure.

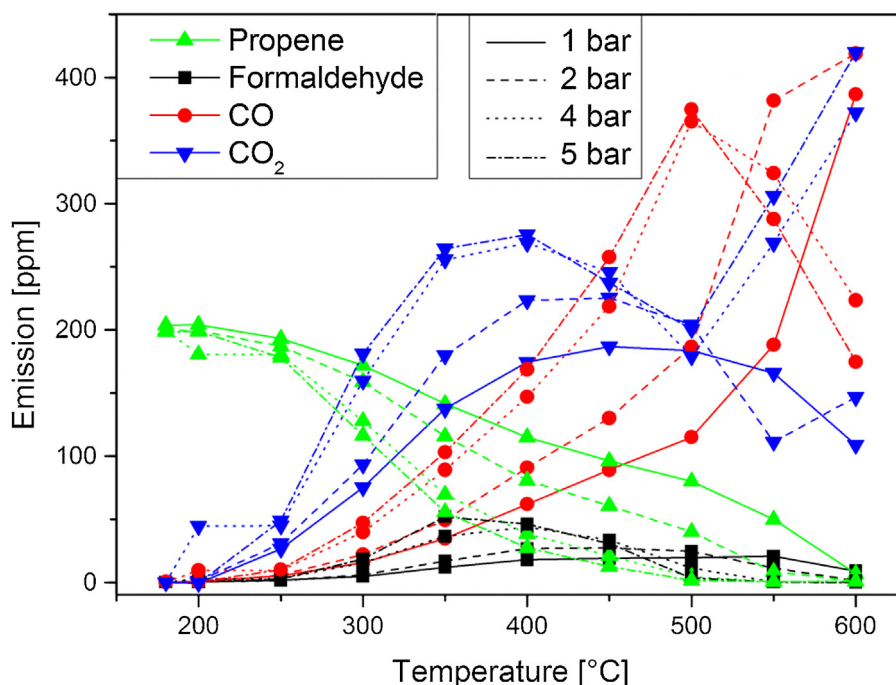
### 3.3. Interaction with SO<sub>2</sub>

The influence of SO<sub>2</sub> on the Standard-SCR-reaction was studied by measuring the DeNO<sub>x</sub>-activity while dosing SO<sub>2</sub> instead of a preliminary sulfation step to achieve more realistic results. The importance of dosing the SCR feed during the sulfation step was outlined by Wijayanti et al. [41] earlier. They reported a higher

deactivation in the additional presence of NH<sub>3</sub> and NO probably due to formation of ammonium sulfur species. A high impact of SO<sub>2</sub> on the DeNO<sub>x</sub>-activity was observed for all pressures at temperatures below 350 °C (Fig. 10). At 250 °C, the deactivating effect reaches a maximum with 60% activity drop relative to the degreened catalyst, independent from the pressure. Recently, Luo et al. [42] also observed this low temperature behavior, which is in line with Zhang et al. [27], who detected the formation of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> at low temperatures on Cu-SAPO-34. Combined with DFT-based calculations, where also (NH<sub>4</sub>)HSO<sub>4</sub> is suggested to form close to the Cu-sites, this can explain the deactivation at low temperatures [43]. As these compounds decompose at around 350 °C and the catalyst



**Fig. 8.** Fast-SCR activity (left, filled symbols) and N<sub>2</sub>O formation (right, open symbols) of the degreened Cu-SSZ-13 with and without dosing C<sub>3</sub>H<sub>6</sub>; solid line – 1 bar, dashed line – 2 bar, dotted line – 4 bar, dash-dotted line – 5 bar. Feed: 0/200 ppm C<sub>3</sub>H<sub>6</sub>, 250 ppm NO, 250 ppm NO<sub>2</sub>, 500 ppm NH<sub>3</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O in N<sub>2</sub>.



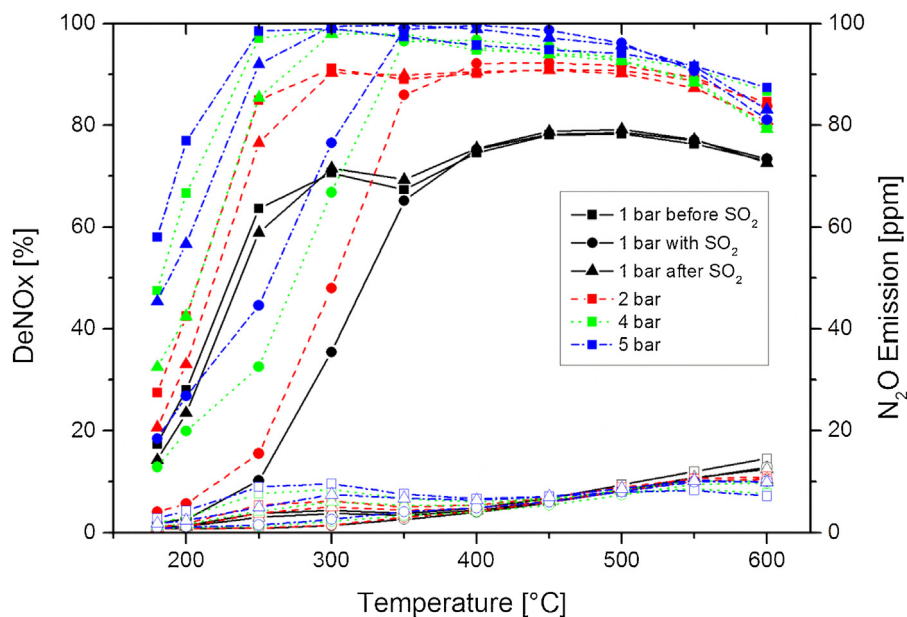
**Fig. 9.** Emission of carbonaceous compounds during Fast-SCR with C<sub>3</sub>H<sub>6</sub> of the degreened Cu-SSZ-13; solid line – 1 bar, dashed line – 2 bar, dotted line – 4 bar, dash-dotted line – 5 bar. Feed: 200 ppm C<sub>3</sub>H<sub>6</sub>, 250 ppm NO, 250 ppm NO<sub>2</sub>, 500 ppm NH<sub>3</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O in N<sub>2</sub>. CO<sub>2</sub> concentration calculated from C-balance.

is mainly affected below this temperature, these compounds are suggested to have the highest impact at low temperatures. Interestingly, the formation of N<sub>2</sub>O is strongly suppressed by the presence of SO<sub>2</sub>, which might be due to poisoning of N<sub>2</sub>O-selective Cu-sites [41,44]. The temperature region between 350 and 450 °C does not show an influence of the presence of SO<sub>2</sub> on the DeNOx-activity. Only above 500 °C the activity decreases slightly at 4 and 5 bar.

After heating up the sample to 600 °C in an SO<sub>2</sub>-free atmosphere, the testing procedure was repeated without SO<sub>2</sub> to check the regenerating effect and possible permanent poisoning. As there was almost no influence observed in the high temperature range, no

major changes were expected by the regeneration step. The small changes at the highest temperature which had been caused by SO<sub>2</sub>, could not be regenerated, instead they show the same activity and formation of N<sub>2</sub>O as under poisoning conditions. This effect could be caused by a more stable sulfur-containing species, which can only be decomposed at temperatures above 600 °C [25]. In order to prevent a possible ageing and to retain a good comparability with earlier experiments, the catalyst was not exposed to temperatures higher than 600 °C. In the low temperature region below 350 °C, a clear regenerating effect is observed. The activity is almost fully recovered at 1 bar. At increased pressure, the activity is com-





**Fig. 10.** Standard-SCR activity (left, filled symbols) and  $\text{N}_2\text{O}$  formation (right, open symbols) of the degreened Cu-SSZ-13 before, with and after dosing  $\text{SO}_2$ . Feed: 0/20 ppm  $\text{SO}_2$ , 500 ppm NO, 500 ppm  $\text{NH}_3$ , 10%  $\text{O}_2$ , 5%  $\text{H}_2\text{O}$  in  $\text{N}_2$ .

pletely regenerated only at 300 °C, whereas at lower temperatures an incomplete recovery indicates permanent poisoning. In this case, the formation of  $\text{N}_2\text{O}$  is again disproportionately low, suggesting a selectivity change of the reaction pathways due to poisoning of one type of active Cu-site.

#### 4. Conclusions

In this study, the influence of increased pressure on the catalytic activity of the SCR-catalyst Cu-SSZ-13 has been examined for the first time. In addition, the effect of propene and sulfur species as possible poisons has been studied in combination with the impact of pressure variation.

The pressure has been varied from 1 to 5 bar, simulating conditions in front of a turbocharger. An increase in pressure resulted in an improved Standard-SCR-activity especially at low temperatures and less pronounced at higher temperatures. On the one side, this may be due to a higher residence time. Comparison of NO oxidation in the empty reactor, over the catalyst and numerical simulations demonstrated that the observed effect is mainly caused by a higher  $\text{NO}_2$ -fraction resulting from pressure induced reactions in the gas phase. As the activity was already high under Fast-SCR-conditions, only small enhancing effects could be observed at low temperatures. A decreased activity at high temperatures was traced back to  $\text{NH}_3$  consumption in the gas phase and a higher residence time at increased pressure. These observations show that gas phase reactions have to be taken into account under these conditions. As the SCR-catalyst would be positioned upstream of the Diesel oxidation catalyst, it is exposed to less  $\text{NO}_2$  and therefore the Standard-SCR receives a higher importance than the Fast-SCR. To further understand the behavior of the reactants, detailed kinetic modeling of the reactions occurring both in the gas phase and on the washcoat need to be conducted in the future. Performing the SCR test at higher pressures uncovered also a moderate deactivation of the Cu-SSZ-13 catalyst, which has to be investigated in further studies.

The additional dosage of propene showed only a small and temporary impact on the SCR-activity, which decreased by an almost constant level of a few percent over the entire temperature range. Propene was mainly oxidized to CO and  $\text{CO}_2$ , which was hardly

influenced by the presence of the SCR-mixture. Full SCR-activity can be regained after propene turn-off with no need for further regeneration steps, suggesting a competitive adsorption of propene and the SCR-gases. The gain from higher temperature and increased pressure during pre-turbine application was higher than the small activity loss during hydrocarbon poisoning. For pressures above 4 bar a pronounced drop in SCR-activity was observed at high temperatures, as propene starts to react with the SCR-gas mixture with consumption of ammonia and  $\text{NO}_2$ . As highly efficient engines produce emission gases at lower temperature, high temperatures will become less important in the future with a higher focus on low temperature activity.

In contrast to propene, which influenced the SCR-activity at all temperatures, the presence of  $\text{SO}_2$  only had an impact up to 350 °C. A complete reactivation was not possible for the strong activity drop observed at low temperatures. This effect was even more pronounced at increased pressure and might be due to the rather limited reactivation obtained at lower temperatures, is responsible for the deactivation. Since the exposure to  $\text{SO}_2$  is independent from the position of the catalyst within the exhaust gas aftertreatment system, it cannot be avoided without replacing sulfur containing fuel and lubricants.

To further understand the behavior of the Cu-SSZ-13 at elevated pressures, detailed kinetic modeling of the reactions occurring both in the gas phase and on the washcoat needs to be conducted similar to former work on vanadia-based catalysts [45]. Moreover, the deactivation of the catalyst as well as the impact of a more realistic gas composition, e.g. further hydrocarbons, and also of soot accumulation need to be studied in more detail.

#### Acknowledgements

We thank Dr. Thomas Bergfeldt (IAM-AWP, KIT) for elemental analysis. DBU and BMBF (05K10VK1, 05K13VK3) are acknowledged for financial support. ABA and OD acknowledge funding by DFG via SFR/TRR 150. JDG acknowledges KIT for financial support to build up the new high pressure unit.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2016.06.005>.

## References

- [1] I. Nova, E. Tronconi, Urea-SCR Technology for DeNO<sub>x</sub> After Treatment of Diesel Exhausts, Springer, New York, 2014.
- [2] T.V. Johnson, SAE Int. J. Engines 8 (2015) 1152–1167.
- [3] J.S. McEwen, T. Anggara, W.F. Schneider, V.F. Kispersky, J.T. Miller, W.N. Delgass, F.H. Ribeiro, Catal. Today 184 (2012) 129–144.
- [4] F. Gao, J. Kwak, J. Szanyi, C.H.F. Peden, Top. Catal. 56 (2013) 1441–1459.
- [5] F. Gao, E.D. Walter, M. Kollar, Y. Wang, J. Szanyi, C.H.F. Peden, J. Catal. 319 (2014) 1–14.
- [6] C. Paolucci, A.A. Verma, S.A. Bates, V.F. Kispersky, J.T. Miller, R. Gounder, W.N. Delgass, F.H. Ribeiro, W.F. Schneider, Angew. Chem. Int. Ed. 53 (2014) 11828–11833.
- [7] L. Olsson, K. Wijayanti, K. Leistner, A. Kumar, S.Y. Joshi, K. Kamasamudram, N.W. Currier, A. Yezerets, Appl. Catal. B: Environ. 174–175 (2015) 212–224.
- [8] T.V.V. Janssens, H. Falsig, L.F. Lundegaard, P.N.R. Vennestrom, S.B. Rasmussen, P.G. Moses, F. Giordano, E. Borfecchia, K.A. Lomachenko, C. Lamberti, S. Bordiga, A. Godiksen, S. Mossin, P. Beato, ACS Catal. 5 (2015) 2832–2845.
- [9] T. Günter, H.W.P. Carvalho, D.E. Doronkin, T. Sheppard, P. Glatzel, A.J. Atkins, J. Rudolph, C.R. Jacob, M. Casapu, J.-D. Grunwaldt, Chem. Commun. 51 (2015) 9227–9230.
- [10] M.N. Subramaniam, V. Joergl, P. Keller, O. Weber, T. Toyoshima, C.D. Vogt, SAE Tech. Paper (2009) (2009-01-1276).
- [11] O. Kröcher, M. Elsener, M.-R. Bothien, W. Dölling, MTZ Worldw. 75 (2014) 46–51.
- [12] C. Brüstle, D. Tomazic, M. Franke, MTZ Ind. 01 (2013) 62–70.
- [13] M.N. Subramaniam, C. Hayes, D. Tomazic, M. Downey, C. Bruestle, SAE Int. J. Engines 4 (2011) 106–116.
- [14] V. Joergl, P. Keller, O. Weber, K. Mueller-Haas, R. Konieczny, SAE Int. J. Fuels Lubr. 1 (2008) 82–95.
- [15] J.M. Luján, V. Bermúdez, P. Piqueras, Ó. García-Afonso, Energy 80 (2015) 599–613.
- [16] A. Kumar, K. Kamasamudram, A. Yezerets, SAE Int. J. Engines 6 (2013) 680–687.
- [17] E. Tronconi, I. Nova, F. Marchitti, G. Koltsakis, D. Karamitros, B. Maletic, N. Markert, D. Chatterjee, M. Hehle, Emiss. Control Sci. Technol. 1 (2015) 134–151.
- [18] K.G. Rappé, Ind. Eng. Chem. Res. 53 (2014) 17547–17557.
- [19] Q. Ye, L. Wang, R.T. Yang, Appl. Catal. A (2012) 427–428, 24–34.
- [20] I. Heo, Y. Lee, I.-S. Nam, J.W. Choung, J.-H. Lee, H.-J. Kim, Micropor. Mesopor. Mat. 141 (2011) 8–15.
- [21] L. Ma, W. Su, Z. Li, J. Li, L. Fu, J. Hao, Catal. Today 245 (2015) 16–21.
- [22] D.J. Kim, J. Wang, M. Crocker, Catal. Today 231 (2014) 83–89.
- [23] I. Bull, W.-M. Xue, P. Burk, S.R. Boorse, W.M. Jaglowski, G.S. Koermer, A. Moini, J.A. Patchett, J.C. Dettling, M.T. Caudle, US Patent (2015) US 2015/0132206 A1.
- [24] Y. Cheng, C. Montreuil, G. Cavataio, C. Lambert, SAE Tech. Paper (2009), 2009-01-0898.
- [25] A. Kumar, M.A. Smith, K. Kamasamudram, N.W. Currier, H. An, A. Yezerets, Catal. Today 231 (2014) 75–82.
- [26] M. Shen, H. Wen, T. Hao, T. Yu, D. Fan, J. Wang, W. Li, J. Wang, Catal. Sci. Technol. 5 (2015) 1741–1749.
- [27] L. Zhang, D. Wang, Y. Liu, K. Kamasamudram, J. Li, W. Epling, Appl. Catal. B: Environ. 156–157 (2014) 371–377.
- [28] T. Günter, D. Doronkin, A. Boubnov, H. Carvalho, M. Casapu, J.-D. Grunwaldt, Top. Catal. (2015), <http://dx.doi.org/10.1007/s11244-016-0561-7>.
- [29] B. Ravel, M. Newville, J. Synchrotron Radiat. 12 (2005) 537–541.
- [30] O. Deutschmann, S. Tischer, C. Correa, D. Chatterjee, S. Kleditzsch, V.M. Janardhanan, N. Mladenov, H.D. Minh, H. Karadeniz, M. Hettel, DETCHEM Software package, Karlsruhe, 2014.
- [31] A.A. Konnov, J. De Ruyck, Combust. Sci. Technol. 149 (1999) 53–78.
- [32] A.A. Konnov, J. De Ruyck, Combust. Flame 124 (2001) 106–126.
- [33] J. Warnatz, Rate coefficients in the C/H/O system, in: W.C. Gardiner (Ed.), Combustion Chemistry, Springer, New York, NY, US, 1984, pp. 197–360.
- [34] S.Y. Joshi, A. Kumar, J. Luo, K. Kamasamudram, N.W. Currier, A. Yezerets, Appl. Catal. B: Environ. 165 (2015) 27–35.
- [35] T.C. Watling, M.R. Ravenscroft, G. Avery, Catal. Today 188 (2012) 32–41.
- [36] J.M. Luján, J.R. Serrano, P. Piqueras, Ó. García-Afonso, Energy 80 (2015) 614–627.
- [37] M. Hori, N. Matsunaga, N. Marinov, P. William, W. Charles, Symp. (Int.) Combust. 27 (1998) 389–396.
- [38] B. Heyberger, F. Battin-Leclerc, V. Warth, R. Fournet, G.M. Côme, G. Scacchi, Combust. Flame 126 (2001) 1780–1802.
- [39] R.T. Pennington, M.C. Fullington, US Patent (1992) US 5117011.
- [40] J.O. Chae, J. Electrostat. 57 (2003) 251–262.
- [41] K. Wijayanti, K. Leistner, S. Chand, A. Kumar, K. Kamasamudram, N.W. Currier, A. Yezerets, L. Olsson, Catal. Sci. Technol. (2016), <http://dx.doi.org/10.1039/C1035CY01288K>.
- [42] J. Luo, D. Wang, A. Kumar, J. Li, K. Kamasamudram, N. Currier, A. Yezerets, Catal. Today 267 (2015) 3–9.
- [43] C. Li, First-principle modeling of SO<sub>x</sub> poisoning in SSZ-13 [abstract], in: 24th North American Meeting, Pittsburgh, 2015.
- [44] O. Mihai, C.R. Widyastuti, S. Andonova, K. Kamasamudram, J. Li, S.Y. Joshi, N.W. Currier, A. Yezerets, L. Olsson, J. Catal. 311 (2014) 170–181.
- [45] C. Hauck, T. Rammelt, R. Gläser, O. Deutschmann, Pre-Turbo SCR, Abschlussbericht (final report), FVV Vorhabens 1120, vol. 1032, Frankfurt am Main/Germany (2013).